

Tunable Far Infrared Studies of Molecular Parameters in Support of Stratospheric Measurements

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Abstract of Research Objectives:

The purpose of this research is to make precise, fully line-resolved measurements of molecular parameters that are necessary for the analysis of spectra obtained in far infrared field measurement programs. These measurements make it possible to accurately analyze the data from field measurements to obtain atmospheric concentration profiles of key trace gases involved in the ozone chemistry.

The research objectives include: measurements of pressure broadening of molecular lines of OH, O₂, O₃, HCl, and H₂O, their temperature dependences and, when possible, the pressure-induced frequency shifts of the lines; measurements of line positions of radical species, such as HO₂.

This research is done in collaboration with K. M. Evenson and D. A. Jennings, National Institute for Standards and Technology, Boulder, CO

Summary of Progress and Results:

Progress to date in this research includes the following studies:

OH Pressure broadening measurements have been made on the hyperfine-split OH lines at 3.551 THz, including: pressure broadening by He and H₂ as functions of temperature from 77 K to 300 K and; pressure broadening by N₂ and O₂ as functions of temperature from 210 K to 300 K. Pressure broadening of the 1.838 THz OH lines by the same gases has been measured at room temperature.

HO₂ The positions of 13 rotational lines of HO₂ have been measured between 2.5 to 5.9 THz, including transitions from levels with K_a as high as 5. A parameterized Hamiltonian is currently being fitted to the new measured positions to provide an improved set of molecular constants for HO₂.

HCl The pressure broadening and shifting of the 83.39 cm⁻¹ (2.500 THz) line of H³⁵Cl at room and stratospheric temperatures have been measured.

O₂ Air- and oxygen-broadening of the 61.32 and 117.87 cm⁻¹ O₂ rotational lines have been measured at stratospheric temperatures.

Publications are currently being prepared on OH, O₂, and HCl.

FAR INFRARED SPECTROSCOPY: ATMOSPHERIC PHYSICS

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ABSTRACT

Ultra high resolution far Infrared laser spectra of molecules of atmospheric importance yield accurate frequencies of their rotational transitions and accurate broadening coefficients. The frequencies are used to identify these species in the atmosphere, and the broadening coefficients are used in determining their absolute concentrations. Two different spectroscopic techniques are used: laser magnetic resonance (LMR) and tunable far infrared (TuFIR) spectroscopy.

PROGRESS AND RESULTS

Far infrared spectra of atmospheric molecules are used to identify species whose atmospheric emission spectra have been observed. Researchers at Harvard College Observatory and at Istituto di Ricerca Elettromagnetica CNR, Italy are making such measurements using high altitude balloon borne Fourier transform spectrometers. O_2 , OH, and HNO_3 spectra have previously been measured; during the past two years, CO, HCl, and HF (1), and HD (2) frequencies were published; and the publication on the HO_2 spectra is in preparation.

Line broadening coefficients have been determined for a number of different transition of various molecules with various collisional partners. These coefficients are necessary to determine the absolute concentrations of the molecule from its emission spectra. The data is also used in determining the pointing direction of the telescopes used in taking the emission data. Previously, a few HCl and OH transitions were measured, and, now, an important O_2 transition broadening coefficient has been reported (3). Measurements of broadening of various transitions of OH, O_2 , and HCl have been completed and the publications are in preparation.

We plan to extend the spectral frequency measurements to other molecules and to measure the broadening coefficients of a number of molecules including temperature dependences of some.

Publications

1. Accurate Rotational Constants of CO, HCl, and HF: Spectral Standards for the 0.3 to 6 THz (10 to 200 cm^{-1}) Region, I.G. Nolt, J.V. Radostitz, G. DiLonardo, K.M. Evenson, D.A. Jennings, K.R. Leopold, M.D. Vanek, L.R. Zink, A. Hinz, and K.V. Chance, J. of Mol. Spectrosc. 125, 274-287.
2. Frequency Measurement of the $J = 1 \leftarrow 0$ Rotational Transition of HD, K.M. Evenson, D.A. Jennings, J.M. Brown, L.R. Zink, K.R. Leopold, M.D. Vanek, and I.G. Nolt, submitted to Ast. Phy. J. Lett., 330, L135-6.
3. Air and Oxygen-Broadening Coefficients for the O_2 Rotational Line at 60.46 cm^{-1} , D. A. Jennings, K.M. Evenson, M.D. Vanek, I.G. Nolt, J.V. Radostitz, and K.V. Chance, Geophysical Research Lett. 14, 722-725.

A. Title: Laboratory Studies of Vibration-Rotation Lineshapes of Atmospheric Constituents

B. Investigator and Institution:

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C. Abstract of Research Objectives

The purpose of this research is to improve our understanding of the spectra of atmospheric constituents important for satellite remote sensing. In particular, investigations that support the CLAES (Cryogenic Limb Array Etalon Spectrometer) and ISAMS (Improved Stratospheric and Mesospheric Sounder) instruments on UARS (Upper Atmosphere Research Satellite) are being pursued. One of the main goals of this work is to study the 791 cm^{-1} Q branch of CO_2 used by CLAES for temperature retrievals. Particular attention is being paid to the effects of line mixing on this Q branch and on other CO_2 bands. Most of the Q branch experimental studies are performed with a tunable diode laser spectrometer.

D. Summary of Progress and Results

A considerable number of spectra of the 791 cm^{-1} CO_2 Q branch used by CLAES for temperature and pressure sounding have been recorded using four different lasers. Spectra of the Q-branch from Q(2) through Q(28) over a wide pressure range were obtained as well as spectra of 70% of the R-branch lines between R(2) and R(32). These measurements show that the line strengths reported in the AFGL HITRAN database are too high by 17%. This difference is much larger than the 3% accuracies required for the CLAES experiment. These spectra also exhibit line mixing which can be accounted for with a scaling law approximation for rotational relaxation in CO_2 .

The line strengths in this band were determined from the diode laser spectra using a new method we developed for this work. Diode laser spectra at low frequencies (such as 791 cm^{-1}) can be severely broadened by the laser emission profile. We have found that the most accurate way to account for this instrument distortion is to use a modified equivalent width method that is described in the first journal publication listed below.

The development of line mixing models appropriate for atmospheric radiative transfer codes has continued. Methods to minimize numerical problems that arise when incorporating line mixing in standard radiative transfer codes have been developed and are being incorporated into GENLN2, the new atmospheric radiative transfer code developed by David Edwards at Oxford.

Curtis Rinsland (NASA/Langley) and I have observed line mixing in the 1932 cm^{-1} CO_2 Q branch in the SpaceLab 3 ATMOS spectra. This work represents the first test of my line mixing formalism at low temperatures.

Spectra of line mixing in a CO_2 Q branch over a wide temperature range (210K to 350K) have been recorded using our tunable diode laser spectrometer. We found that the simple scaling law model for line mixing successfully models the observed spectra over the complete temperature range. However, a different scaling law had to be used for each temperature. We are now trying to develop a single scaling law that is accurate over the complete temperature range.

Far wing CO_2 lineshapes are important for the ISAMS experiment on UARS. Previous attempts to compare experimentally observed far wing lineshapes to theory have failed due to the neglect of line mixing. This has stopped attempts to develop physically meaningful far wing lineshapes for atmospheric spectra. We have analyzed existing laboratory observations of far wing CO_2 lineshapes in the $4.3\text{ }\mu\text{m}$ R-branch of CO_2 and found that a reasonable physical model for the far wing lineshape is possible if line mixing is included.

Ab-initio calculations of line mixing are needed to put my phenomenological formulation of line mixing on firmer ground. Unfortunately, good intermolecular potentials (and computer codes) exist

only for linear molecule - atom collisions, so ab-initio calculations for $\text{CO}_2\text{-N}_2$ collisions are not possible at present. However, calculations of line mixing for $\text{CO}_2\text{-Ar,He}$ collisions are possible. I have recorded Q-branch spectra of CO_2 broadened by Ar and He in order to compare to ab-initio calculations by Sheldon Greene of NASA/Goddard Institute for Space Studies. His calculations agree very closely with my phenomenological scaling law calculations of line mixing for the $\text{CO}_2\text{-He}$ system. However, both calculations disagree significantly with the observed spectra in the wing of the Q branch for unknown reasons.

E. Journal Publications (1988-1989):

L. L. Strow and L. Zheng, **A Modified Equivalent-Width Technique for Diode-Laser Line Strength Measurements**, accepted for publication, J. Quant. Spectrosc. Rad. Trans., 1989.

C. P. Rinsland and L. L. Strow, **Line Mixing Effects in Solar Occultation Spectra of the Lower Stratosphere: Measurements and Comparisons with Calculations for the $1932\text{ CO}_2\text{ cm}^{-1}$ Q Branch**, Applied Optics, 28, 457-464, 1989.

L. L. Strow, **Line Mixing in Infrared Atmospheric Spectra**, Invited Paper, Modeling of the Atmosphere, Critical Reviews of Optical Science and Technology Series, Laurence S. Rothman, Editor, SPIE Vol. 928, 194-212, 1988.

L. L. Strow and A. S. Pine, **Q-Branch Line Mixing in N_2O : Effects of l-Type Doubling**, J. Chem. Physics, 89, 1427-1434 (1988).

L. L. Strow and D. Reuter, **The Effect of Line Mixing on Atmospheric Brightness Temperatures Near $15\text{ }\mu\text{m}$** , Applied Optics, 27, 872-878 (1988).

A. Title of Research Task

Laboratory Spectroscopic Measurements Relevant to Upper Atmospheric Research. (Grant-in-Aid No. NAGW-1238)

B. Investigator and Institution

Prasad Varanasi, Professor of Atmospheric Science, Institute for Atmospheric Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2300.

C. Abstract of Research Objectives

Infrared spectroscopic research that is being performed in our laboratory consists of measurements of absolute intensities and air-broadened half-widths of infrared spectral lines of atmospheric trace gases. The measurements are designed to yield data that are needed in the interpretation of many atmospheric remote sensing experiments conducted by NASA employing air-borne, balloon-borne, and satellite-borne infrared spectrometers. Our laboratory data are obtained at low temperatures relevant to the atmosphere using cryogenically cooled absorption cells and with the ultra-high spectral resolution ($\sim 10^{-4} \text{ cm}^{-1}$) of a tunable diode laser spectrometer.

D. Summary of Progress and Results

Intensity measurements were performed in the 720.8 cm^{-1} Q-branch of $^{12}\text{C}^{16}\text{O}_2$, since the $15 \mu\text{m}$ bands have been important in atmospheric spectroscopic studies such as remote sensing and temperature sounding of the atmosphere as well as in the study of the enhanced greenhouse effect brought about by the increase in the atmospheric concentration of CO_2 . Several of the past and proposed future satellite-borne temperature sounding experiments employ infrared spectral channels designed specifically to isolate the $15 \mu\text{m}$ lines of CO_2 . The accuracy of these sounders depends not only on the precision of the instruments employed but also on the reliability of the available spectroscopic database. Therefore, our purpose was to examine the validity of the currently adapted spectroscopic parameters, in particular, the intensities in the 720.8 cm^{-1} band. The accuracy of our results for the absolute intensities of the lines between 718.9499 cm^{-1} and 719.8319 cm^{-1} in the Q-branch and of the R(1) line at 722.3644 cm^{-1} to be about 98 % based upon the systematic errors and instrumental precision of our experiment.

Nitrous oxide is a trace constituent in the terrestrial atmosphere with an infrared-active fundamental band at $7.78 \mu\text{m}$. Since this strong absorption band is located in the so-called window region of the thermal infrared spectrum of the atmosphere, it is effective in enhancing the greenhouse effect and the resulting perturbation on the global climate. It is also important in atmospheric chemistry involving nitrogen, especially, in the production of odd nitrogen species of NO_x which are involved in the catalytic cycles that destroy O_3 directly. N_2O is recognized as the major source of NO_x in the stratosphere. Because $^{14}\text{N}_2^{16}\text{O}$ is produced in the troposphere and is destroyed in the stratosphere, it serves as a dynamical tracer of the motion of tropospheric air into the lower stratosphere. On account of this distinction, several studies of this molecule were featured in the 1987 Airborne Antarctic Ozone Experiment. The correlation between O_3 and N_2O as well as the relationship between CN and N_2O has also been studied as an important aspect of the airborne measurements that were performed on the so-called Ozone Hole in Antarctica. The thermal infrared lines of $^{14}\text{N}_2^{16}\text{O}$ have also been assigned special significance in the remote sensing of the Antarctic stratosphere with airborne Fourier transform spectrometers. In all of the above applications, accurate knowledge of the absolute intensities of the spectral lines in the ν_1 -fundamental band of $^{14}\text{N}_2^{16}\text{O}$ has become necessary. Interpretation of the N_2O spectra obtained with the airborne spectrometers also requires data on the air-broadened half-widths at low temperatures relevant to the Antarctic stratosphere, in which the temperatures can be as low as 190 K. The above stated applications point toward the need for laboratory data on the intensities and air-broadened half-widths of rotational lines in the ν_1 -fundamental of $^{14}\text{N}_2\text{O}$ and their temperature dependence at temperatures relevant to the terrestrial atmosphere. Therefore, we have performed measurements on several lines between 1240 and 1280 cm^{-1} using our tunable diode laser spectrometer. Line intensities have been determined along with N_2 -, O_2 -, and air-broadened line widths at several temperatures between 150 and 296 K. The values of the exponent n which describes the variation of the line width with temperature were found to be practically identical in N_2 -broadening and O_2 -broadening.

Laboratory data on the air-broadened halfwidths of spectral lines in the ν_4 -fundamental band of $^{12}\text{CH}_4$ at $7.66 \mu\text{m}$ and on their variation with temperature are necessary in the analysis of the thermal infrared spectrum of the atmosphere. We have, therefore, measured at several temperatures between 100 and 296 K the intensities and half-widths of P(5), P(6) and P(9) multiplets located between 1240 and 1280 cm^{-1} in broadening by N_2 , O_2 , Ar, and air. The temperature dependence and the relative magnitudes of the line widths of the A, E, F species of rotational lines were examined for each of the broadening cases.

We consider the present set of low temperature measurements on the lines of CH_4 and N_2O not only to be the most accurate to come out of our laboratory to date, but also, to the best of our knowledge, to be the first ever measured at low

temperatures employing the ultra-high spectral resolution ($\sim 10^{-4} \text{ cm}^{-1}$) of a tunable diode laser spectrometer. In view of the important role the spectral lines of $^{13}\text{CH}_4$ assume in remote sensing of the atmosphere, we have also measured the intensities and collision-broadened line widths in the ν_4 -fundamental band of $^{13}\text{CH}_4$ at 295 K. Ar, N_2 , O_2 , and air were chosen as the broadening gases.

Determination of the abundance of CH_3D in the atmosphere by analysing the observed spectra requires accurate laboratory data on the absolute intensities and air-broadened half-widths of the lines of CH_3D at temperatures that are relevant to the atmosphere. Therefore, we have measured at several temperatures between 100 and 296 K the intensities and half-widths of several multiplets in the ν_3 and ν_6 fundamentals of $^{12}\text{CH}_3\text{D}$. The temperature dependence of intensities and of half-widths of lines in N_2 -, O_2 -, Ar-, air-broadening has been determined.

We have also measured the pressure-induced shifts of several lines of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$ and $^{14}\text{N}_2^{16}\text{O}$ located between 1265 and 1350 cm^{-1} and of their temperature dependence, which we are the first ever to have measured.

We have recently completed measurements of the spectral transmittance of CF_2Cl_2 and CFCl_3 using ultra-high spectral resolution of the diode laser spectrometer and the moderate-resolution of a grating spectrometer at several temperatures between 200 and 296 K. We have determined accurately the temperature dependence of the absorption coefficient in the important thermal infrared bands of these two CFCs. These measurements are also first of their kind.

E. Journal Publications and a Ph.D. Dissertation

Varanasi, P. and Chudamani, S. : Measurement of Pressure-Induced Shifts of Infrared lines with a Tunable Diode Laser. *JQSRT* **41**, 173-176, 1989.

Varanasi, P. and Chudamani, S. : Absolute Intensity Measurements in the ν_4 - Fundamental Band of $^{12}\text{CH}_4$ at Planetary Atmospheric Temperatures. *JQSRT*, **41**, 345-349, 1989.

Varanasi, P. and Chudamani, S. : Measurements of Collision-Broadened Line Widths in the ν_4 - Fundamental Band of $^{12}\text{CH}_4$ at Low Temperatures. *JQSRT*, **41**, 335-343, 1989.

Varanasi, P. and Chudamani, S. : Tunable Diode Laser Measurements of line widths in the ν_1 - Fundamental Band of $^{14}\text{N}_2^{16}\text{O}$ at atmospheric temperatures. *JQSRT*, **41**, 351-357, 1989.

Varanasi, P. and Chudamani, S. : Line Strength Measurements in the ν_1 - Fundamental Band of $^{14}\text{N}_2^{16}\text{O}$ using a Tunable Diode Laser. *JQSRT*, **41**, 359-362, 1989.

Varanasi, P. and Chudamani, S. : Line Intensity Measurements in the ν_3 - and ν_6 - Fundamental Bands of $^{12}\text{CH}_3\text{D}$ at Low Temperatures Relevant to Planetary Atmospheric Observations. *J. Mol. Spectrosc.*, **134**, 440-444, 1989.

Varanasi, P. and Chudamani, S. : Linewidth Measurements in the Thermal Infrared Bands of $^{12}\text{CH}_3\text{D}$ at Planetary Atmospheric Temperatures. *Appl. Opt.* **28**, 2119-2122, 1989.

Varanasi, P. and Chudamani, S. : Measurements of Collision-broadened Line Widths in the $7.66 \mu\text{m}$ Band of $^{12}\text{CH}_4$ at Temperatures Relevant to the Atmosphere. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Intensity and Line Width Measurements in the ν_4 - Fundamental Band of $^{13}\text{CH}_4$. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Infrared Spectroscopic Measurements on Atmospheric Trace Gases at Relevant Temperatures. Invited Contribution in *IRS 88 : Current Problems in Atmospheric Radiation*. J. LeNoble and J. F. Geleyn, Eds., A. Deepak Publishing, 392-397, 1989.

Varanasi, P. and Chudamani, S.: The Temperature Dependence of Lineshifts, Linewidths and Line Intensities of Methane at Low Temperatures. *JQSRT* (in press).

Varanasi, P. and Chudamani, S. : Intensity Measurements in the 720.8 cm^{-1} Q-Branch of $^{12}\text{C}^{16}\text{O}_2$. *J. Geophys. Res.* (in press).

Varanasi, P. and Chudamani, S. : Measurements of the Spectral Absorption Coefficient in the Thermal Infrared Bands of CFC-11 and CFC-12 at Low Temperatures. *JQSRT* (submitted for publication).

Kratz, D. P. and Varanasi, P. : A Study of the Radiative Effects of CFCl_3 and CF_2Cl_2 . *J. Geophys. Res.* (submitted for publication).

Chudamani, S. : *Infrared Spectroscopic Measurements on Planetary Atmospheric Gases*. Dissertation submitted for the Ph. D degree in Atmospheric Sciences, State University of New York at Stony Brook, May 1989.